Niobium oxide prepared through a novel supercritical-CO_2-assisted method as highly active heterogeneous catalyst for the synthesis of azoxybenzene from aniline

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Supporting information

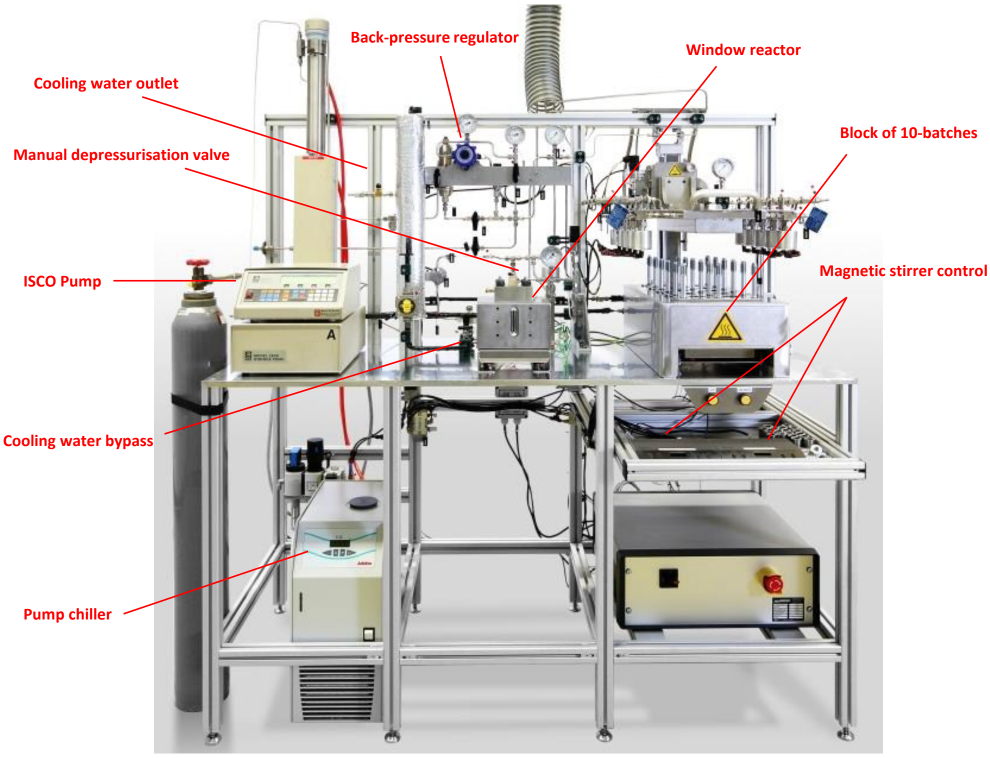


Fig. S1 High-throughput $scCO_2$ reactor

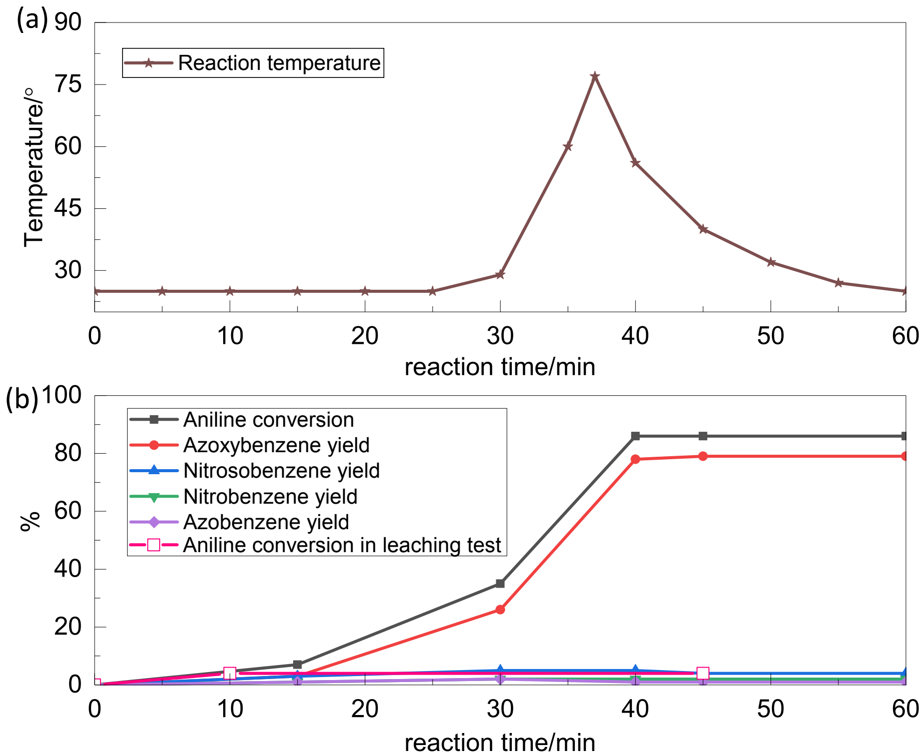


Fig. S2 (a) Temperature of the reaction mixture as a function of time. (b) Conversion of 20 mmol aniline over Nb_2O_5-$scCO_2$ catalyst. Reaction conditions: 20 mmol aniline, 28 mmol 30 wt % H_2O_2, 10 mmol anisole, 10 mL ethanol, 10 mg catalyst, room temperature, 45 min.

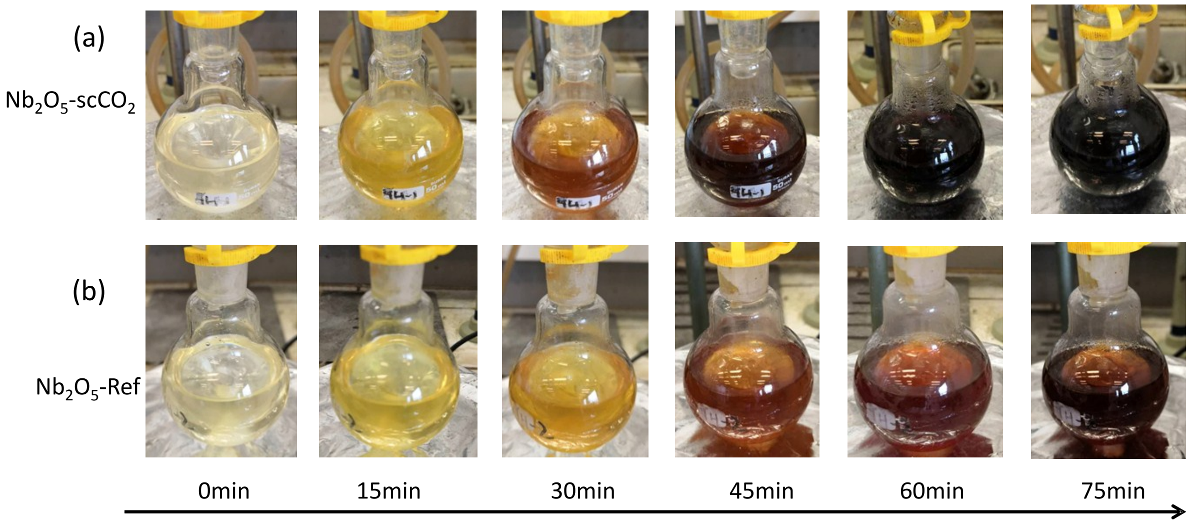


Fig. S3 Conversion of 50 mmol aniline with (a) Nb_2O_5-scCO_2 and (b) Nb_2O_5-Ref catalyst as a function of time. Reaction conditions: 50 mmol aniline, 70 mmol 30 wt% H_2O_2, 25 mmol anisole, 25 mL ethanol, 10 mg selected catalyst, room temperature. Note: the change in colour can be qualitatively correlated to the formation of the reaction products [nitrosobenzene (light yellow), nitrobenzene (light yellow), azobenzene (red) and azoxybenzene (light brown)].

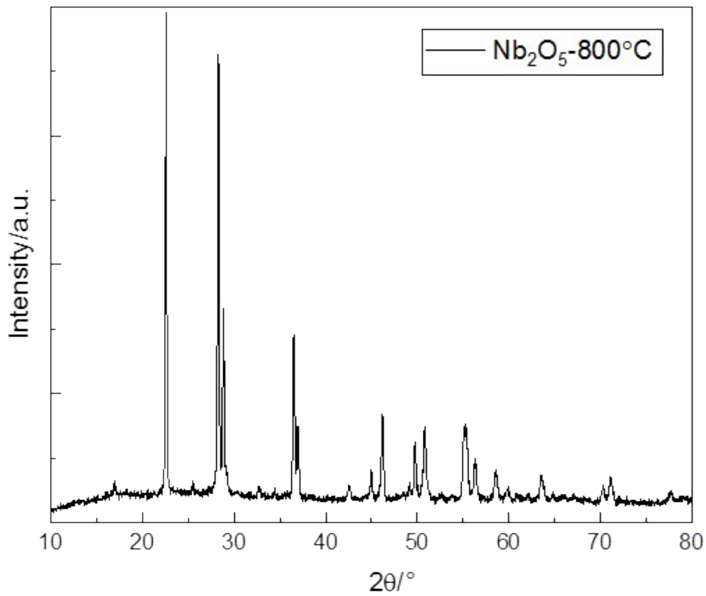


Fig. S4 XRD pattern of Nb_2O_5-800^oC.

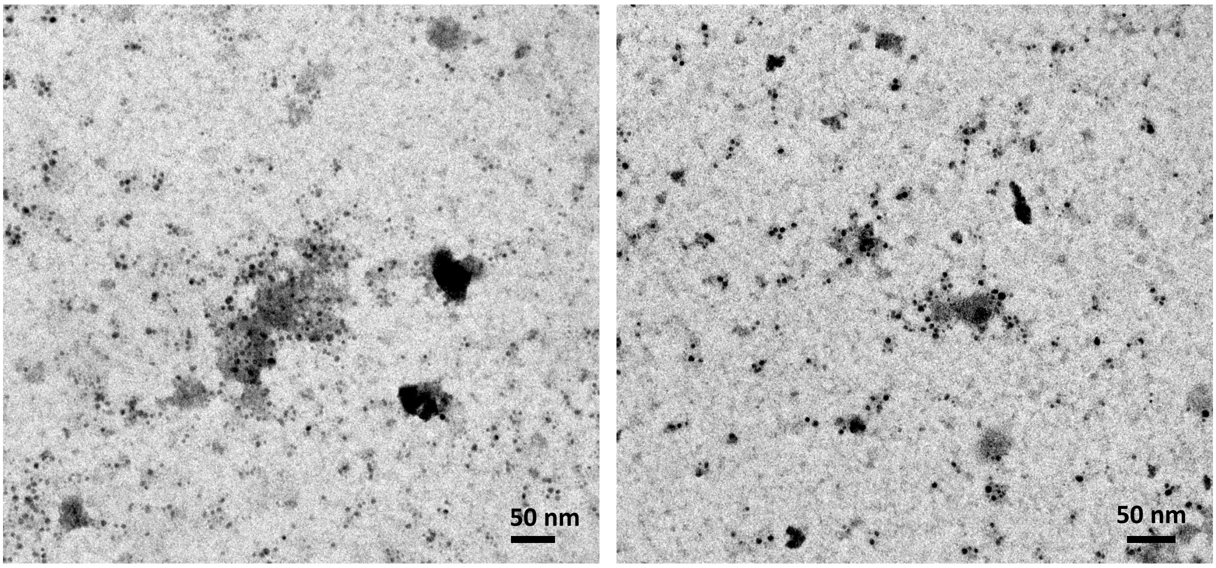


Figure S5 TEM images of Nb_2O_5-scCO_2.

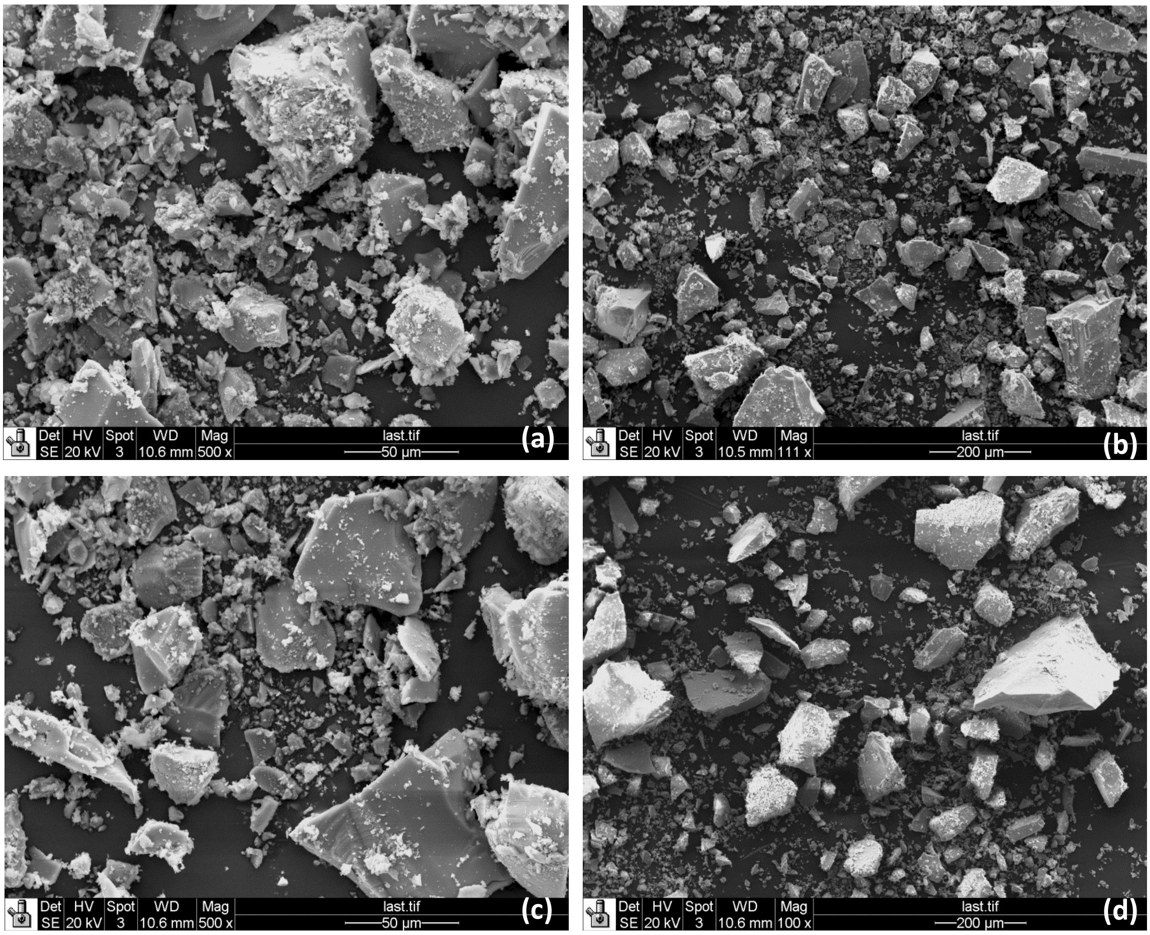


Figure S6 SEM images of (a), (b) Nb_2O_5-scCO_2 and (c), (d) Nb_2O_5-Ref.

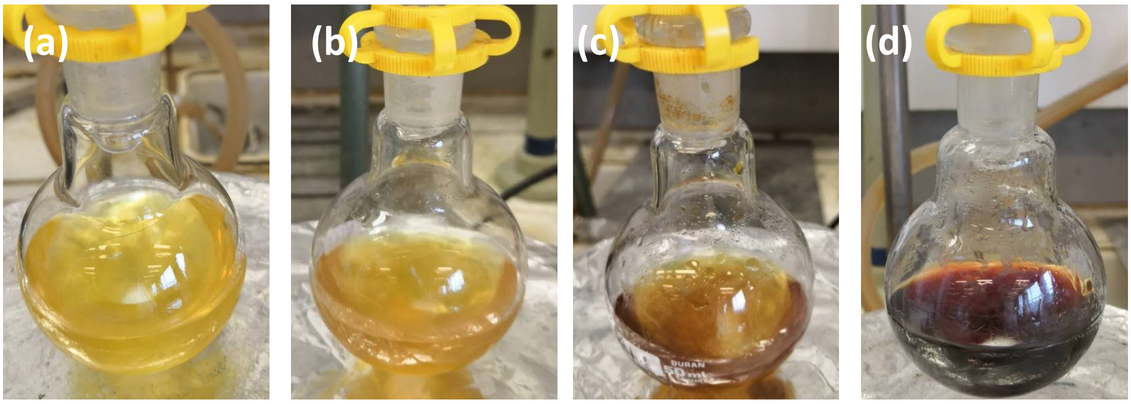


Fig. S7 Effect of H_2O_2 concentration on aniline conversion. Reaction conditions: 20 mmol aniline, 28 mmol (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, (d) 50 wt% H_2O_2, 10 mmol anisole, 10 mL ethanol, 10 mg Nb_2O_5-$scCO_2$ catalyst, room temperature, 25 min. Note: the change in colour can be qualitatively correlated to the formation of the reaction products [nitrosobenzene (light yellow), nitrobenzene (light yellow), azobenzene (red) and azoxybenzene (light brown)].

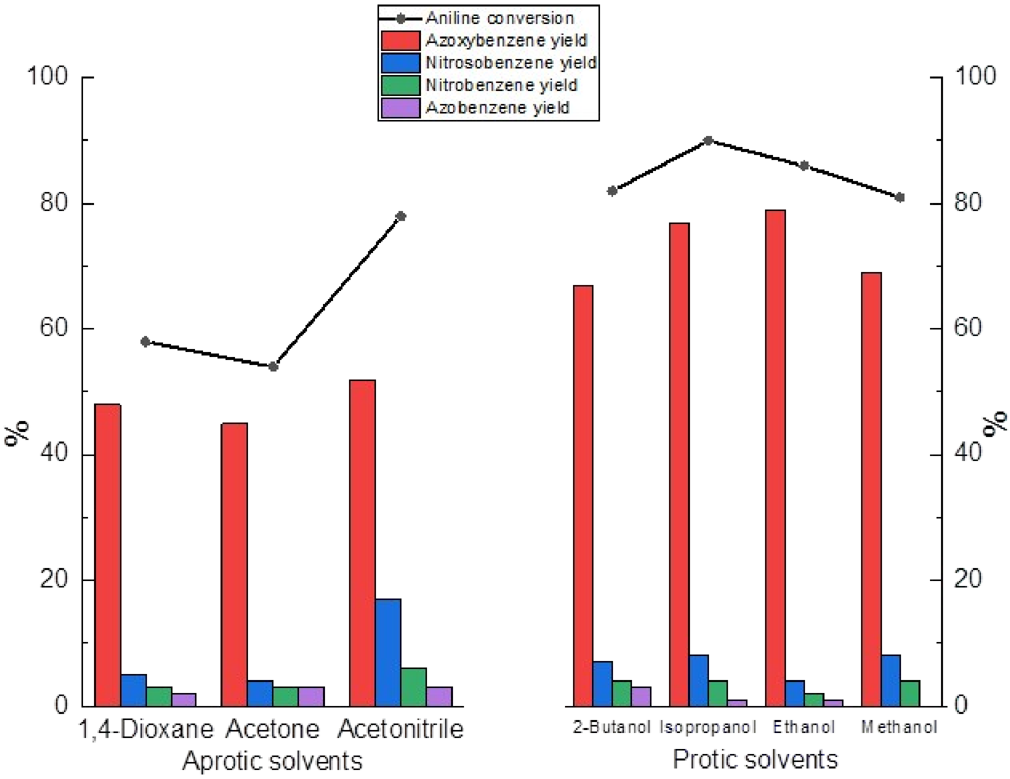


Fig. S8 Effect of solvents on aniline conversion. Reaction conditions: 20 mmol aniline, 28 mmol 30 wt% H_2O_2, 10 mmol anisole, 10 mL solvent, 10 mg Nb_2O_5-$scCO_2$ catalyst, room temperature, 45 min.

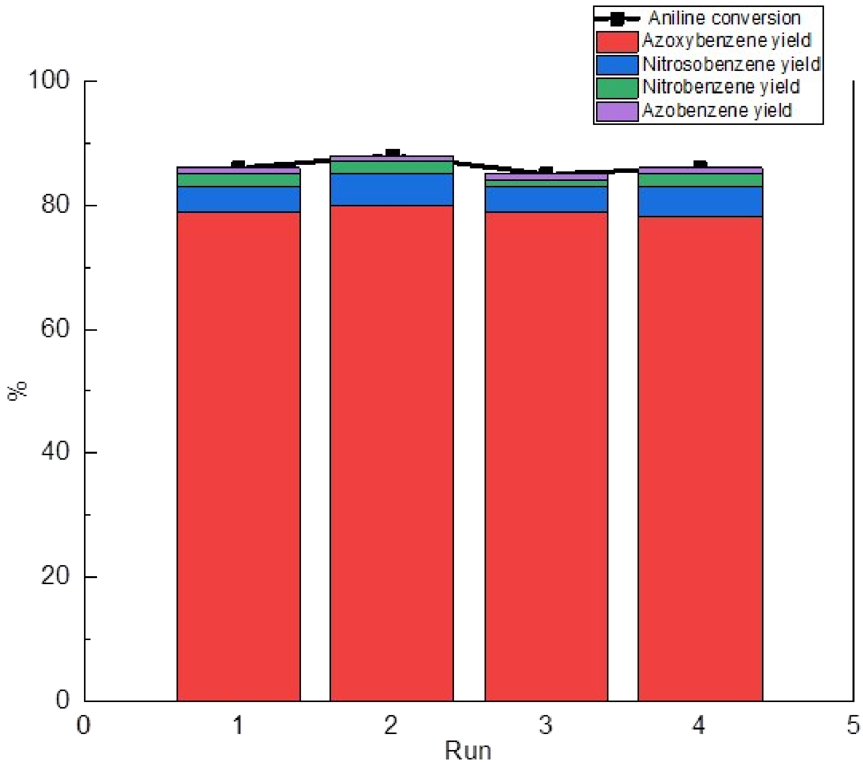


Fig. S9 Reusability test of the Nb_2O_5-$scCO_2$ catalyst in oxidative coupling of aniline with H_2O_2. Reaction conditions: 20 mmol aniline, 28 mmol 30 wt% H_2O_2, 10 mmol anisole, 10 mL ethanol, 10 mg Nb_2O_5-$scCO_2$ catalyst, room temperature, 45 min.

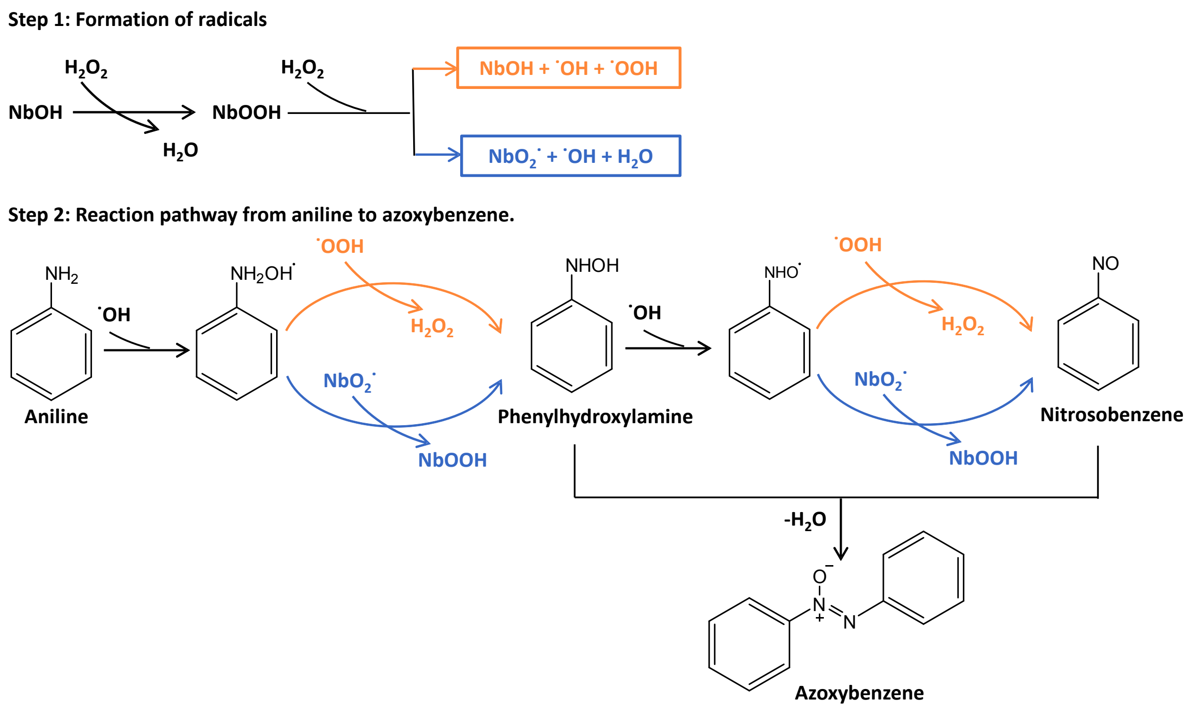
Table S1 Literature overview of heterogeneous catalysts for the oxidative coupling of aniline with H_2O_2.

Ref.	Catalyst	Catalyst loading, $(R_{c/s})^a$	Aniline: H_2O_2	T (ºC)	Reaction time (h)	Solvent	Conv. (%)	Yield (%)	Prod $(h^{-1})^b$
This	Nb_2O_5	0.005	1:1.4	RT	0.75	Ethanol	86	79	209
1	TiO_2	0.86	1:3	50	0.5	Methanol	> 99	98	2.3
2	TiO_2	0.013	1:1.7	60	0.75	-	98	96	95
2	P25	0.013	1:1.7	60	0.75	-	52	51	50
3	TiO_2-montmorillonite	0.02	1:1	RT	8	Methanol	50	49	3.1
4	TS-1	0.05	1:0.8	70	3	t-Butanol	N.M.	20	1.2
5	TS-1	0.21	1:1	Reflux	6	Acetone	N.M.	87	0.7
6	Ti-MCM-48	0.02	1:3	50	3	Methanol	N.M.	90	2.0
7	Ti-Beta	0.11	1:0.2	70	3	Acetonitrile	N.M.	8	0.2
8	Co-Si-oxide	0.01	1:2	80	6	Acetonitrile	> 99	> 99	16
9	$CuCr_2O_4$	0.1	1:5	70	10	1,4-Dioxane	78	72	0.7
10	Ag-WO_3	0.1	1:3	RT	24	Acetonitrile	87	79	0.3
11	Cu-CeO_2	0.1	1:3	50	6	Acetonitrile	95	87	1.4
12	NbOOH-FeOOH	0.1	1:11	RT	24	Propanol	> 99	80	0.3
13	Nb-Zn-Al-oxide[c]	0.1	1:2	RT	48	Methanol	95	90	0.2

[a] $R_{c/s}$ is defined as the weight ratio between catalyst and aniline. [b] The productivity is defined as the grams of product generated per gram of catalyst in 1 hour. [c] Photocatalyst, operating under UV irradiation. N.M.: not mentioned.

Table S2 List of chemicals used in this work, and their purity.

Chemical	Purity (%)	Supplier
$NbCl_5$	99	Sigma-Aldrich Co.
Ethanol	100	J.T.Baker
Nb_2O_5-Comm	-	Sigma-Aldrich Co.
TiO_2-P25	-	Sigma-Aldrich Co.
WO_3-Comm	-	Sigma-Aldrich Co.
Aniline	99	Sigma-Aldrich Co.
o-toluidine	99	TCI Europe N.V.
m-toluidine	98	TCI Europe N.V.
p-toluidine	99.6	Sigma-Aldrich Co.
2-ethylaniline	98	Sigma-Aldrich Co.
3-ethylaniline	98	Sigma-Aldrich Co.
4-ethylaniline	98	TCI Europe N.V.
p-anisidine	99	Sigma-Aldrich Co.
benzylamine	99	Sigma-Aldrich Co.
Anisole	99	Acros Organics
H_2O_2	30 wt% in H_2O	Sigma-Aldrich Co.
H_2O_2	50 wt% in H_2O	Sigma-Aldrich Co.
1,4-dioxane	99	Emplura
Acetone	100	Biosolve
Acetonitrile	99.8	Sigma-Aldrich Co.
2-Butanol	99.5	Sigma-Aldrich Co.
Isopropanol	99.7	Sigma-Aldrich Co.
Methanol	100	Biosolve
2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO)	98	Sigma-Aldrich Co.



Scheme S1 Proposed reaction pathway for the oxidative coupling of aniline with H_2O_2 to azoxybenzene over the Nb_2O_5-scCO_2 catalyst.

Reference

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